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3,824,135

## COPPER BASE ALLOYS

Michael J. Pryor, Woodbridge, Stanley Shapiro, New Haven, and Richard D. Lanam, Hamden, Conn., assignors to Olin Corporation  
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6 Claims

### ABSTRACT OF THE DISCLOSURE

The disclosure teaches novel copper base alloys having improved toughness and outstanding resistance to stress corrosion. The copper alloys contain, in weight percentages, from 15 to 30% nickel, from 15 to 30% manganese, an element selected from the group consisting of aluminum from 0.01 to 5%, magnesium from 0.01 to 5%, boron from 0.001 to 0.1%, zinc from 0.1 to 3.5%, tin from 0.01 to 3%, zirconium from 0.01 to 2%, titanium from 0.01 to 2%, chromium from 0.01 to 1%, iron from 0.1 to 5%, cobalt from 0.05 to 1%, and mixtures thereof, together with 0.005 to 0.1% of an element selected from the group consisting of arsenic and antimony, and mixtures thereof.

### BACKGROUND OF THE INVENTION

Copper base alloys are known which contain relatively large amounts of nickel and manganese. Alloys of this type are highly desirable since they are capable of attaining yield strengths in excess of 200 k.s.i. upon aging. In addition, these alloys appear to have reasonable processing qualities and in particular are not quench sensitive.

The presence of a marked aging response to obtain high strengths in copper-nickel-manganese alloys is known. It has been found that different types of precipitation reactions may occur in this alloy system, depending on the aging temperature. For example, aging at a low temperature, such as 350° C., yields a cellular precipitate which nucleates at the grain boundaries and with time grows throughout the entire grain. The cellular precipitate consists of adjacent lamellae of a manganese-nickel rich phase and the copper-rich solid solution. Aging at higher temperatures, such as 450° C., yields mainly finely dispersed, spherical precipitates of the manganese-nickel rich phase within the grains and only a small amount of the cellular precipitate at the grain boundaries.

However, in any event, the presence of a cellular precipitate at grain boundaries is generally found to have deleterious effects on alloy properties, such as fracture toughness and stress corrosion resistance. This is indeed found to be the case in these alloys and is a significant factor in the limited commercial success of these alloys heretofore.

Generally, the copper base alloys used in springs and similar applications rely upon extensive cold work in order to achieve high strengths, for example, greater than 150 k.s.i. 0.2% offset yield strength. However, such extensive cold work imposes severe limitations on the subsequent formability of the alloys.

While known copper-2% beryllium age-hardenable alloys achieve yield strengths in the 150 to 200 k.s.i. range, have good formability in the un-aged condition, and exhibit good performance under stress corrosion conditions, such alloys are characterized as expensive, quench sensitive, and difficult or even dangerous to cast, thus exhibiting difficult processing properties. In contrast, the age-hardenable Cu-Ni-Mn alloys are relatively inexpensive, are not quench sensitive, and are characterized by favorable processing properties, such as being well adapted to hot or cold rolling. However, such alloys of the prior art have been inadequate with respect to toughness and par-

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ticularly with respect to resistance to stress corrosion for especially demanding uses, such as in springs likely to be exposed to a corrosive atmosphere under stress. While significant improvement in these properties was attained in the alloys described in U.S. Pat. 3,712,837, a more beneficial combination of properties remained desirable, particularly with respect to increased resistance to stress corrosion.

Accordingly, it has been highly desirable to develop an alloy within the copper-manganese-nickel alloy system which has increased fracture toughness in combination with significantly improved stress corrosion resistance qualities.

Accordingly, it is a principal object of the present invention to develop an improved copper base alloy containing relatively large amounts of nickel and manganese.

It is an additional object of the present invention to develop an alloy as aforesaid which is capable of obtaining yield strengths in excess of 200 k.s.i. upon aging.

It is a still further object of the present invention to develop an alloy as aforesaid which is readily processed commercially and which is characterized by improved fracture toughness.

It is a still further object of the present invention to provide a copper base alloy with excellent stress corrosion resistance, good ductility, toughness and high yield strength characteristics.

Further objects and advantages of the present invention will appear from the ensuing discussion.

### SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been found that the foregoing objects and advantages may be readily obtained.

The alloy of the present invention consists essentially of from 15 to 30% nickel, from 15 to 30% manganese, and an element selected from the group consisting of aluminum from 0.01 to 5%, magnesium from 0.01 to 5%, boron from 0.001 to 0.1%, zinc from 0.1 to 3.5%, tin from 0.01 to 3%, zirconium from 0.01 to 2%, titanium from 0.01 to 2%, chromium from 0.01 to 1%, iron from 0.1 to 5%, cobalt from 0.05 to 1%, and mixtures thereof, together with 0.005 to 0.1% of an element selected from the group consisting of arsenic, antimony, and mixtures thereof, with the balance essentially copper wherein the nickel to manganese ratio is at least 0.75 and preferably 1.0 or higher.

### DETAILED DESCRIPTION

In accordance with the present invention, the foregoing alloy has been found to obtain surprisingly improved fracture toughness while retaining the excellent strength characteristics of this alloy system.

This enables the attainment of several significant advantages. The alloy of the present invention is an excellent lower priced replacement for beryllium-copper, with increased fracture toughness. The alloy of the present invention achieves levels of fracture toughness approaching high alloy steels which are limited in applicability by poor corrosion resistance. The alloys of the present invention are superior to maraging steels in marine environments since the alloys of the present invention are not susceptible to hydrogen embrittlement. In addition, the alloys of the present invention are characterized by excellent stress corrosion resistance.

In accordance with the present invention, the instant alloys contain from 15 to 30% nickel, and from 15 to 30% manganese. Preferably, both the nickel and manganese contents should range from 15 to 25%. The nickel to manganese ratio must be at least 0.75 and preferably 1.0 or higher.

The nickel and manganese contents have an effect on aging response, yield strength and workability of the alloys. The lower the manganese and nickel content, the slower the aging response and lower the maximum yield strength obtainable upon aging, especially below 15% nickel and manganese. On the other hand, increasing the amount of nickel and manganese has deleterious effects on the workability of the alloys during processing, especially over 30% each of nickel and manganese.

As indicated hereinabove, the preferred nickel to manganese ratio is 1.0 or higher. The maximum aging response is obtained for a given amount of nickel and manganese when the nickel to manganese ratio is about 1.0. If the ratio is less than 1.0, an excess of manganese exists which can have adverse effects on the stress corrosion resistance of the alloy. A ratio greater than about 1.5 generally does not provide sufficiently improved results over a ratio of about 1.0 to justify the higher cost of the nickel.

In addition to the foregoing, the alloy of the present invention contains an element selected from the group consisting of aluminum in an amount from 0.01 to 5.0%, magnesium from 0.01 to 5.0%, boron from 0.001 to 0.1% zinc from 0.1 to 3.5%, tin from 0.01 to 3%, zirconium from 0.01 to 2%, titanium from 0.01 to 2%, chromium from 0.01 to 1%, iron from 0.1 to 5%, cobalt from 0.05 to 1%, and mixtures thereof.

Aluminum, magnesium, and boron act as deoxidizers and assist in the melting of the alloys. Aluminum is the preferred addition since it tends to form a protective oxide coating during melting. When aluminum is used as a deoxidant only, it should be added in an amount from 0.01 to 0.75%, and similarly for magnesium. Furthermore, the aluminum and magnesium may be used as advantageous alloying additions in amounts greater than 0.6% for increased corrosion resistance and fracture toughness. The aluminum when used at the higher levels, also tends to modify the cellular precipitate at the grain boundaries.

When zinc is an added component, it should be present in an amount from 0.1 to 3.5%. Increased amounts of zinc over 3.5% given rise to a decrease in the stress corrosion resistance and fracture toughness. The zinc addition tends to control the grain size, reduce the cellular precipitate at the grain boundaries, alter the morphology of the inclusions, promote sound castings and increase the aging response of the alloy. It is most surprising that so many advantages may be realized from a single alloying addition. The grain size control may be attributed to a fine dispersoid which is present in the zinc containing alloys. The increased aging response is due to an increase in the growth rate of the precipitate. The preferred zinc content is from 1 to 3%.

In addition to the foregoing, several additives are particularly advantageous. Tin is a particularly desirable additive in an amount from 0.01 to 3% and preferably from 0.5 to 2.0%. Tin tends to alter the morphology of the cellular precipitate at the grain boundary.

Zirconium and/or titanium are preferred alloying additions in amounts 0.01 to 2.0% each, and preferably from 0.15 to 0.30% each. These elements tend to effect desirable changes in the morphology and chemistry of inclusions and in the morphology of cellular precipitate at grain boundaries.

In addition, chromium is a desirable addition in an amount from 0.01 to 1.0%, and preferably from 0.15 to 0.30%. Chromium tends to control the grain size and change the morphology and chemistry of inclusions.

Additional desirable alloying additions are cobalt and/or iron. These elements are desirable for providing desired control of grain size. The cobalt may be employed in an amount from 0.05 to 1.0% and preferably from 0.2 to 0.5%, and the iron from 0.1 to 5% and preferably from 0.5 to 1.0%.

The advantageous combination of outstanding resist-

ance to stress corrosion, physical properties such as to enable excellent performance in demanding uses, and desirable formability qualities in the alloys is attained with certainty in accordance with this invention through the further addition of a small but essential proportion of arsenic or antimony or mixture thereof within the range of 0.005 to 0.1% by weight. Such addition has been found to assure the proper control of grain size and the desired dispersion of fine precipitate mostly throughout the interior of the grains, which have been indicated as essential for the desired alloy qualities and performance.

It is noteworthy that such effects of the arsenic and antimony additions differ essentially from those customarily obtained in single phase copper-base alloys. In the latter, the additions have customarily been made to reduce dezincification. If the alloy is not single phase, the general experience has been that no beneficial effect from the addition is found. The alloys of the present invention comprise an age hardening system. They are polyphase in the final heat treated condition. It is, therefore, quite surprising that the addition of arsenic and/or antimony would result in the improved stress corrosion performance noted for these alloys in both industrial and marine environments.

However, single phase copper base alloys containing arsenic and antimony are known to be hot short, exhibiting such limited hot rollability that they must generally be subjected only to cold rolling. In contrast, the alloys of the present invention are hot rollable and are single phase in the hot working temperature range. It is quite surprising that a single phase copper base alloy containing either arsenic and/or antimony in these amounts is hot rollable.

The casting of the alloy of the present invention is not particularly significant. Any convenient method of casting may be employed. Pouring temperatures in the range of about 1000 to 1200° C. are preferably employed, with an optimum pouring temperature in the range of 1050 to 1100° C. The arsenic and/or antimony additions should be as a master alloy prior to pouring, for convenience due to the toxicity of these materials.

Generally, the alloy of the present invention is processed by breakdown of ingot into strip using a hot rolling operation followed by cold rolling and annealing cycles to reach final gage. Preferred properties are obtained using an aging treatment.

The starting hot rolling temperature should be in the range of 700 to 900° C., and preferably 750 to 850° C. The cooling rate from hot rolling should preferably be in excess of 25° C. per hour down to 300° C. in order to avoid precipitation of manganese-nickel rich phases. The cooling rate after 300° C. is not significant. The alloy is capable of cold rolling reductions in excess of 90%, but the cold rolling reduction should preferably be between 30 and 80% in order to control the grain size.

It has been found that an average grain size less than 0.005 mm. is necessary in order to provide optimum stress corrosion resistance. Generally, an average grain size in the alloys of the present invention of less than 0.003 mm. is readily obtained. An average grain size of this order can be obtained by control of the cold rolling reduction, annealing times and annealing temperatures. In general, anneal-temperatures in the range of 550 to 900° C. for at least one minute can give the required grain size, with 10 hours being the practical upper limit and 2 hours being the preferred upper limit. It is preferred to anneal for from five minutes to 2 hours.

After annealing, the material is cooled in excess of 25° C. per hour down to 300° C., as indicated above, and the cold rolling and annealing cycles repeated as desired depending on gage requirements. Generally, from two to four cycles of cold rolling and annealing are preferred.

The present invention will be more readily understandable from a consideration of the following illustrative examples.

## EXAMPLE I

A 10 lb. ingot of an alloy containing 25.0 nickel, 17.0 manganese, 2.0 zinc, 0.5 aluminum, .04 antimony (Alloy A) and the balance copper was prepared in strip form in the following manner. The alloy was melted from elemental constituents except for the antimony which was added as a copper-antimony master alloy and chill cast from 1200° C. into a steel mold. The ingot was soaked

increasing the yield strength level at which the alloy can be used.

## EXAMPLE III

Example II was repeated for Alloy D except that the samples were cold worked 40 and 50% prior to aging. Alloy C was treated with 40% cold work prior to aging for comparison purposes. The data is shown in Table B below.

TABLE A

Solution heat treat plus 25% cold work

| Alloy  | Aging treatment         | 0.2% offset yield strength, k.s.i. | Tensile strength, k.s.i. | Percent elongation, inches | Time to failure—New Haven—days | Time to failure—Daytona—days |
|--------|-------------------------|------------------------------------|--------------------------|----------------------------|--------------------------------|------------------------------|
| A----- | 450° C. X3.5 hours----- | 168.0                              | 178.8                    | 6.5                        | 278                            | 140                          |
| A----- | 450° C. X6.0 hours----- | 183.5                              | 192.5                    | 5.3                        | 69                             | 52                           |
| B----- | 450° C. X5.0 hours----- | 156.1                              | 173.5                    | 10.0                       | 204                            | 4                            |
| B----- | 450° C. X8.0 hours----- | 169.3                              | 185.0                    | 8.8                        | 59                             | 9                            |
| C----- | 450° C. X4.0 hours----- | 158.3                              | 177.5                    | 10.3                       | 81                             | 1 <sup>2</sup>               |
| C----- | 450° C. X8.0 hours----- | 182.0                              | 198.0                    | 6.5                        | 16                             | 1 <sup>2</sup>               |
| D----- | 450° C. X3.5 hours----- | 168.3                              | 179.5                    | 7.0                        | 309                            | 143                          |
| D----- | 450° C. X6.0 hours----- | 184.7                              | 196.5                    | 7.0                        | 81                             | 39                           |

TABLE B

Solution heat treat plus 40% cold work and 50% cold work

| Alloy and condition   | Aging treatment         | 0.2% offset yield strength, k.s.i. | Tensile strength, k.s.i. | Percent elongation, inches | Time to failure—New Haven—days | Time to failure—Daytona—days |
|-----------------------|-------------------------|------------------------------------|--------------------------|----------------------------|--------------------------------|------------------------------|
| 40% cold work:        |                         |                                    |                          |                            |                                |                              |
| C-----                | 450° C. X4.0 hours----- | 168.0                              | 185.0                    | 6.0                        | 52                             | 26                           |
| D-----                | 450° C. X8.0 hours----- | 185.4                              | 195.0                    | 2.0                        | >180                           | >120                         |
| 50% cold work: D----- |                         |                                    |                          |                            |                                |                              |
|                       | 450° C. X8.0 hours----- | 188.3                              | 200.3                    | 4.0                        | >180                           | >120                         |

<sup>1</sup> Samples still in test.

at 845° C. and hot rolled from 1.5" to .250". The hot rolled plate was cold rolled to 0.100" and annealed at 600° C. for 30 minutes. The plate was cold rolled 60% to .040" and annealed at 600° C. for 30 minutes. The material was cold rolled 25% to a final gauge of 0.030". Samples of the 25% cold rolled strip at 0.030" were formed into 90° U-bends by bending a strip 6" long by 1/2" wide around a mandrel so that it permanently forms a 90° bend, and transverse tensile samples were fabricated. The U-bends and tensile specimens were aged for various times at 450° C. After the aging treatment, the U-bends were sprung into jigs which hold the ends of the samples 1" apart. The resulting tensile properties and stress corrosion results are presented in Table A. The tensile results are the average of two transverse samples; the stress corrosion results the average of five U-bends. New Haven, Connecticut, is an industrial environment and Daytona Beach, Florida, a marine environment. Data for a copper-25 nickel-17 manganese-2 zinc alloy (Alloy B) and copper-20 nickel-20 manganese-0.5 Al (Alloy C) are also presented for comparison purposes. These were processed in a similar manner to the antimony containing alloy.

## EXAMPLE II

An alloy containing 25 nickel, 17 manganese, 2 zinc, 0.5 aluminum, 0.04 arsenic (Alloy D) and balance copper was prepared in strip form by a similar practice to that described above. The tensile properties and stress corrosion results are also listed in Table A.

The improvement in the stress corrosion life becomes even more evident when the times to failure in New Haven and Daytona Beach are examined in terms of yield strength. The effect of the antimony and arsenic additions in both New Haven and Daytona Beach is to increase the time to failure at a given yield strength, thus

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A copper base alloy having improved stress corrosion resistance coupled with high strength and good fracture toughness consisting essentially of: from 15 to 30% nickel; from 15 to 30% manganese; an element selected from the group consisting of aluminum from 0.01 to 5%, magnesium from 0.01 to 5%, boron from 0.001 to 0.1%, zinc from 0.1 to 3.5%, tin from 0.01 to 3%, zirconium from 0.01 to 2%, titanium from 0.01 to 2%, chromium from 0.01 to 1%, iron from 0.1 to 5%, cobalt from 0.05 to 1%, and mixtures thereof; and from 0.005 to 0.1% of an element selected from the group consisting of arsenic, antimony and mixtures thereof; balance essentially copper, wherein the nickel to manganese ratio is at least 0.75, said alloy having an average grain size of less than 0.005 mm. and a dispersion of fine precipitate throughout the interior of the grains and characterized by being hot rollable, single phase in the hot working temperature range and polyphase in the heat treated condition.

2. A copper alloy according to Claim 1 wherein the nickel to manganese ratio is from 1.0 to 1.5.

3. An alloy according to Claim 1 wherein both the nickel and manganese contents range from 15 to 25%.

4. An alloy according to Claim 1 containing aluminum in an amount from 0.01 to 0.75%.

5. An alloy according to Claim 1 containing aluminum in an amount from 0.01 to 5.0%, zinc from 0.1 to 3.5% and antimony from 0.005 to 0.1%.

6. An alloy according to Claim 1 containing aluminum in an amount from 0.01 to 5.0%, zinc from 0.1 to 3.5% and arsenic from 0.005 to 0.1%.

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CHARLES N. LOVELL, Primary Examiner

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